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LOW-MELTING GLASSES BASED ON BORATE SYSTEMS

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The results of analyzing systems of low-melting glasses and their application areas based on published data are used to select an optimum system. The melting properties of low-melting glasses based on the borate system $ZnO – SrO – B_2O_3$ are studied. The dependences of the main properties of glasses (TCLE, softening temperature, microhardness, chemical resistance to water) on their compositions are determined. The optimum low-melting glass compositions with required physicochemical and technological parameters are identified.

Low-melting glasses are used as solders in vacuum engineering and electronics, in the production of integrated circuits, as protective coatings for electronic elements, for depositing various patterns and inscriptions on glass articles, and for glass-glass and glass-metal seals. Low-melting glass seals are homogeneous and free from stresses, provided the TCLE is appropriately selected.

Low-melting noncrystallizing glasses intended as fluxes in the production of silicate paints for glass articles have been mostly synthesized in the systems $PbO – B_2O_3 – SiO_2$ and $Na_2O – PbO – B_2O_3 – SiO_2$ [1]. The mass content of PbO in them ranges from 50 to 78% and their softening temperature varies from 380 to 470°C.

The most intense research on low-melting glasses was carried out in 60s – 80s in the context of the development of glass-ceramic cements and glass cements commonly used for soldering parts of color TV tubes, for glass-to-metal seals, multilayer integrated circuits, or for sealing multiple window panes. The research was mainly focused on the systems $PbO – ZnO – B_2O_3$ and $PbO – ZnO – B_2O_3 – SiO_2$ [2]. According to the data in [3], the formation of extremely low-melting compounds was registered in the first system, such as $2PbO \cdot ZnO \cdot B_2O_3$ with an incongruent melting point of 575°C, $2PbO \cdot 2ZnO \cdot B_2O_3$ with incongruent melting at 730°C, and $4PbO \cdot 2ZnO \cdot 5B_2O_3$ melting at 680°C. Evidently, the eutectics in this system serving as the basis for glass-forming compositions are even more fusible. However, the content of PbO in the specified compositions is around 71.5 – 79.0% [2].

Solder glasses with softening temperatures of 370 – 380°C as well have a high content of PbO ranging from 75.0 to 77.5% [4].

A high content of toxic lead oxide in low-melting glasses is undesirable, as it creates environmental problems in melting fluxes and in the application of glasses.

Therefore, one of the goals of the present study is the development of low-melting noncrystallizing glasses with a decreased PbO content. Borate systems without SiO_2 or with a very low content of SiO_2 were the basis for these glasses.

An earlier study corroborated the positive effect of ZnO on the properties of borate glasses. The lowest-melting eutectic in the binary system $ZnO – B_2O_3$ with a melting point of 961°C contains 65.5% ZnO and 34.5% B_2O_3 [3] (or molar content of 62 and 38%, respectively), i.e., the molar ratio $ZnO : B_2O_3$ in this eutectic is approximately 1.6. The glass-forming compositions with a molar content of 45 – 63% ZnO and 37 – 55% B_2O_3 are precisely positioned near this eutectic. The TCLE of the glass approaching the eutectic and containing 59.9% ZnO is equal to $41.1 \times 10^{-7} K^{-1}$ [5]. Despite the low melting point of this glass, it cannot be used as a flux, primarily due to its very low TCLE. The composition had to be corrected by introducing an oxide with a larger cation, for instance, SrO.

Glass formation in the $SrO – B_2O_3$ system was registered within the molar range of 23 – 42% SrO and 58 – 77% B_2O_3, i.e., with a significantly lower quantity of SrO than that of ZnO.

Data on the ternary system $ZnO – SrO – B_2O_3$ are given only in [6]: the glass-formation area is within the range of 0 – 60% ZnO, 0 – 40% SrO, and 35 – 70% B_2O_3 (Fig. 1). This system was chosen as the basis for experimental compositions, considering the prevalence of ZnO content over SrO. To increase the fusibility and stability of the vitreous state, small constant additives of Li_2O, PbO, SiO_2, and Al_2O_3 ($\Sigma R_mO_n = 20\%$) were additionally introduced.

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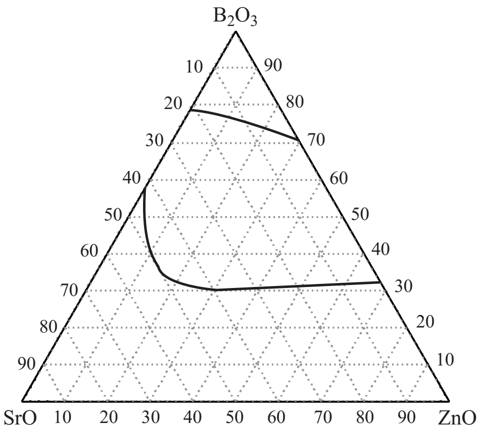

Fig. 1. Glass-formation area in system ZnO – SrO – B_2O_3 [6].

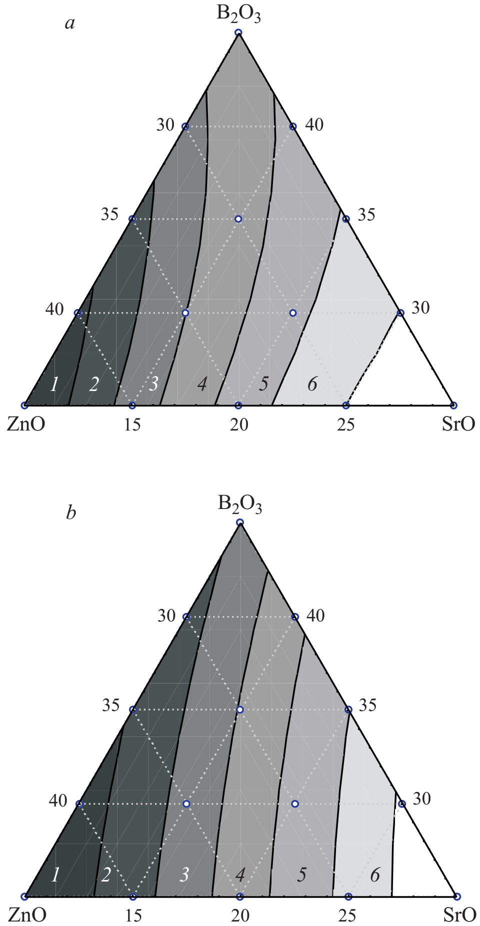

Fig. 2. Dependence of the softening temperature (*a*) and TCLE (*b*) on glass composition ($\Sigma R_mO_n = 20\%$): (*a*) *1*, *2*, *3*, *4*, *5*, and *6*) 451, 463, 474, 486, 479, and 509°C, respectively; (*b*) *1*, *2*, *3*, *4*, *5*, and *6*) 73.5×10^{-7}, 74.7×10^{-7}, 75.8×10^{-7}, 76.9×10^{-7}, 78.1×10^{-7}, and 79.2×10^{-7}, respectively.

The glasses were melted in porcelain crucibles in a silit electric furnace at temperatures of 1000 – 1100°C with an exposure at the maximum temperatures for 20 – 30 min. All

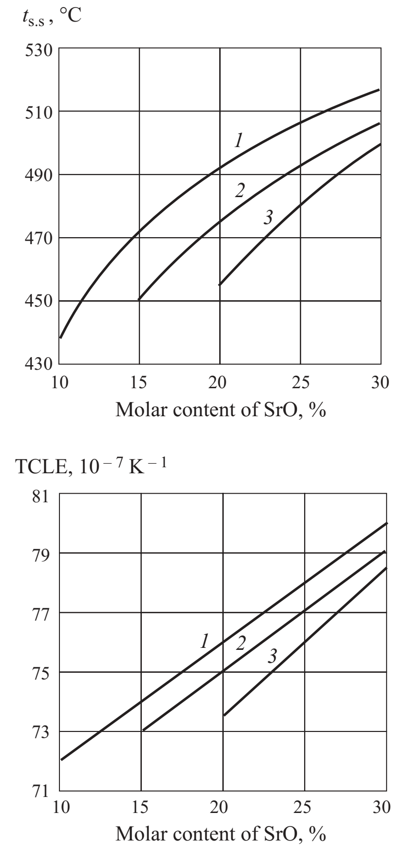

Fig. 3. The effect of SrO on softening temperature $t_{s.s}$ and TCLE of glasses: *1*, *2*, and *3*) 25, 30, and 5% B_2O_3, respectively.

glasses were sufficiently well melted. The most fusible were glasses with an increased ZnO content. To determine the dependence of the properties of glass on its composition, we investigated such properties as TCLE (a vertical quartz dilatometer), softening start temperature $t_{s.s}$ (using DTA curves and the method of metallic rod indentation), microhardness (PMT-3 instrument), and chemical resistance to water (the powder method).

Figure 2 indicates summarized data on the variation of TCLE and $t_{s.s}$ of glasses in the system considered. It has been found that the TCLEs of glasses are within $(72 – 80) \times 10^{-7}$ K^{-1} and the $t_{s.s}$ is 440 – 520°C. Equal yield curves were constructed using the Statistica software package for the integrated Window-98 environment.

It can be seen that glasses with the minimum $t_{s.s}$ (440 – 450°C) are located in the high-zinc region of the system. Increasing B_2O_3 content in the considered area of the system has an insignificant effect on these parameters. The effect of individual components is more visible in Fig. 3.

The TCLE and the $t_{s.s}$ are most perceptibly increased by SrO and, accordingly, lowered by ZnO. An increase in B_2O_3 lowers the TCLE, but less significantly than an increased concentration of ZnO. All curves have a smooth shape, which points to the stability of structural groups and the absence of perceptible coordination transformations. The

glasses with minimum values of $t_{s.s}$ are located in the high-zinc part of the system, close to the eutectic ratio of $ZnO : B_2O_3$ in the respective binary system.

There are few data on the structure and properties of borate glasses with a molar content of 30 – 45% B_2O_3, including two RO oxides. In particular, the TCLEs of glasses in the $CaO – ZnO – B_2O_3$ system are specified in [6]. With 20% CaO and 40% ZnO the TCLE of glasses is equal to $62.3 \times 10^{-7} K^{-1}$ and with 40% CaO and 20% ZnO it is $67.5 \times 10^{-7} K^{-1}$. In the system considered we have registered somewhat higher values, close to $75.0 \times 10^{-7} K^{-1}$, which is due not only to introducing SrO with a larger cation than the CaO cation, but also to the effect of the additives.

According to the data in [7], with molar R_2O content over 45% and B_2O_3 below 55% an intense destruction of $[BO_4]$ groups and, accordingly, an increase in the number of $[BO_3]$ groups take place, with the oxides of large cations intensifying this process. It can be expected that the content of $[BO_4]$ groups in experimental glasses containing 25 – 45% B_2O_3 is insignificant as well and the main structural lattice is made up by groups $[BO_3]$. The constancy of the structural state of boron is corroborated by the absence of significant deviations on the curves of the property-composition dependence.

The experimental values of the microhardness of experimental glasses are within the limits of 4400 – 7000 MPa. The minimal microhardness values characterizing the overall strength of the bonds in glasses (and the $t_{s.s}$) are seen in the high-zinc compositions as well.

It is established that the experimental glasses are resistant to water. Their weight loss in boiling (the granular method) for 1 h is equal to 0.04 – 0.10%, i.e., their chemical resistance to water is 99.00 – 99.96 %.

The variation bounds of the physicochemical properties of glasses in the system $ZnO – SrO – B_2O_3$ (+ R_mO_n) are indicated below.

Physicochemical properties of glasses

Softening start temperature, °C	440 – 520
TCLE, $10^{-7} K^{-1}$	72.4 – 80.3
Microhardness, MPa	4400 – 7000
Chemical resistance to water, %	99.00 – 99.96

Thus, the optimum compositions are located in the high-zinc range with a minimum B_2O_3 content, since these low-melting glasses have a minimum softening temperature with a corresponding TCLE, which determines the properties of fluxes. The optimum glass compositions can be recommended for use as low-melting fluxes for paints, solders, and seals.

REFERENCES

1. V. M. Ivanova and G. V. Kochetkova, *Treatment of Glass Articles Using Silicate Paints, Inform. Review* [in Russian], VNIIÉSM, Moscow (1978).
2. A. I. Berezhnoi, *Glass Ceramics and Photoglass Ceramics* [in Russian], Mashinostroenie, Moscow (1981).
3. N. A. Toropov, V. P. Barzakovskii, V. V. Lapin, and N. N. Kurtseva, *Phase Diagram of Silicate Systems, A Reference Book, Issue 1* [in Russian], Nauka, Moscow – Leningrad (1965).
4. A. I. Berezhnoi, *Glass Ceramics and Photoglass Ceramics* [in Russian], Mashinostroenie, Moscow (1960).
5. O. V. Mazurin, M. V. Strel'tsina, and T. P. Shvaiko-Shvaikovskaya, *Properties of Glasses and Glass-Forming Melts, A Reference Book, Vol. II* [in Russian], Nauka, Leningrad (1975).
6. O. V. Mazurin, M. V. Strel'tsina, and T. P. Shvaiko-Shvaikovskaya, *Properties of Glasses and Glass-Forming Melts, A Reference Book, Vol. III* [in Russian], Nauka, Leningrad (1975).
7. F. D. Bray, "A study of glass structure using the magnetic nuclear resonance method," in: *Vitreous State* [Russian translation], Nauka, Moscow – Leningrad (1965).